

## Optical Identification of Cu Doped ZnSe Nanoparticles

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### ABSTRACT

In nanomaterials the length of reduced dimension has to be smaller than the phase coherence length for electrons in the materials. The size dependent luminescence, blue shift in the optical absorption spectrum, enhance oscillator strength, nonlinear optical effects, geometrical strength, melting point, magnetic properties etc. are all affected by particle size. Wide bandgap semiconductors can be doped either by n-type or p-type, but not both, because of compensation by native defects. The chemical synthesis of Cu doped ZnSe nanocrystals slowly grow to a final size is dependent on the synthesis conditions. During particle growth samples are extracted to study the luminescence as a function of particle size. Quantum size effects are observed to influence the Cu doped ZnSe related luminescence emissions. In order to study the structural properties and size, X-ray diffraction patterns, absorption spectra and also photoluminescence of Cu doped ZnSe nano particle have been recorded.

**Keywords:** Nano particle, polyvinyl pyrrolidone (PVP), photoluminescence, photo detection, and quantum size effect.

### INTRODUCTION

The discoveries and innovations in materials development are essential without which the newer technologies may not come to fruition. Presently human efforts are to develop new materials by the use of technological ability, to design and alter material dimensions are in nanometer scale. Nano-particles exhibit physical and chemical properties different from either the individual molecules or the bulk; hence these have attracted an enormous attention

during the past two decades. ZnSe is a direct band gap semiconductor belonging to the II-VI groups. Several physical and chemical synthesis techniques are available for ZnSe. P-ZnSe can be obtained by doping of Li, N, Cu, Ag IP<sup>1-5</sup> by different methods, while Cl, Al<sup>6</sup> can be used for n type dopant in ZnSe.

The growth rate of nanocrystals is strongly depending upon doping concentration, capping agent concentration and synthesis temperature. Quantum size effects are observed to influence both the

ZnSe and Cu related luminescence emission<sup>7</sup>. Measurements on bulk ZnSe crystals doped with copper have revealed the presence of green and red emission bands, which have been assigned to recombination of electrons in shallow traps with different Cu<sup>2+</sup> centers<sup>8-10</sup>. The Cu<sup>2+</sup> related emission wavelength in nanocrystalline ZnS of ZnSe semiconductor particles is expected to shift to higher shift to higher energies in smaller particles. In some recent studies on ZnSe:Cu this has indeed been observed<sup>11,12</sup>. In the synthesis procedure used, the ZnSe particles grow slowly and properties of the ZnSe:Cu were studied as a function of particle size with samples taken at different concentration.

The structural and optical properties as well as its good chemical and mechanical stability recommends ZnSe as a semiconductor well suited for optoelectrical applications, such as photodetection or solar energy conversion. The recognition of strongly size and shape dependent physical or chemical properties of nanostructure materials has stimulated efforts towards the fabrication of nanocrystals in a systematic and controlled way. Chemically synthesized nanostructures and their assembly are of fundamental importance due to their unique dimension dependent properties and their potential applications as building blocks in nanoelectronics, nano-optonics, nano-sensors, actuators, and in biology. Recently much interest has been created in the preparation and assembly of semiconductor QDs due to their narrow and intensive emission spectra, continuous absorption band, high chemical and photo bleaching stability, processability and surface functionality.<sup>13</sup>

Thaddeus *et al.* had synthesized Cu(II) doped ZnSe nanoparticles using molecular cluster precursors<sup>14</sup>. The Cu(II) dopant had the effect of quenching the ZnSe band edge emission, yet only weak emission from Cu(II) centers was observed. An X-ray Absorption Fine Structure (XAFS) experiment was performed on the Cu (II) doped ZnSe nanoparticles.

The wide band gap of ZnSe and significantly large binding energy, make this an ideal choice as an inorganic passivation shell for a variety of semiconductor core/shell nanocrystals. In order to improve the stability and emission properties of the semiconductor core nanocrystals with relatively narrow band gap and for efficient room temperature exciton devices with improve temperature characteristics<sup>15</sup>.

ZnSe is also attractive host for the formation of doped nanocrystals. Several novel applications have been presented which require size, shape and phase control of ZnSe nanostructured materials. There are several reports describing various synthesis route for ZnSe nanoparticles, most of the reports yielded the cubic (Zinc blende) structure of ZnSe with a less amount of hexagonal (Wurtzite) structure. So far, various ZnSe nanostructures including quantum dots, nanowires and nanoribbons<sup>16</sup> have been synthesized.

## SYNTHESIS OF ZnSe:CU NANOPHOSPHORS

The methods used for synthesis of nanoparticles can be broadly classified into three types, namely physical method, chemical methods and hybrid method Fig.1. The physical methods are based on subdivision of bulk metals, including

mechanical crushing or pulverization of bulk metals, discharge between metal electrodes, and so on. Metal nanoparticles thus produced are usually large in size and have wide size distribution. The chemical methods are based on reduction of metal ions or decomposition of precursors to form atoms, followed by aggregation of the atoms. Nanoparticles prepared by chemical methods have usually a narrow size distribution<sup>17</sup>.

In recent years, attention is focused on materials obtained by soft chemistry routes. Chemical methods are characterized by a complete and homogeneous mixing of

the solutions of starting compound to the molecular or atomic level. These form a category in which one has larger control of synthesis parameters like reactants concentration, pH, solvents etc. These are comparatively simpler and less expensive with more yields in a relatively shorter time. Here, the chemical salts are reacted in presence of organic or inorganic capping agent to form the nanoparticles. By comparing properties of the materials obtained from different routes, colloidal precipitation was found to be better for producing efficient luminescent nanophosphors.

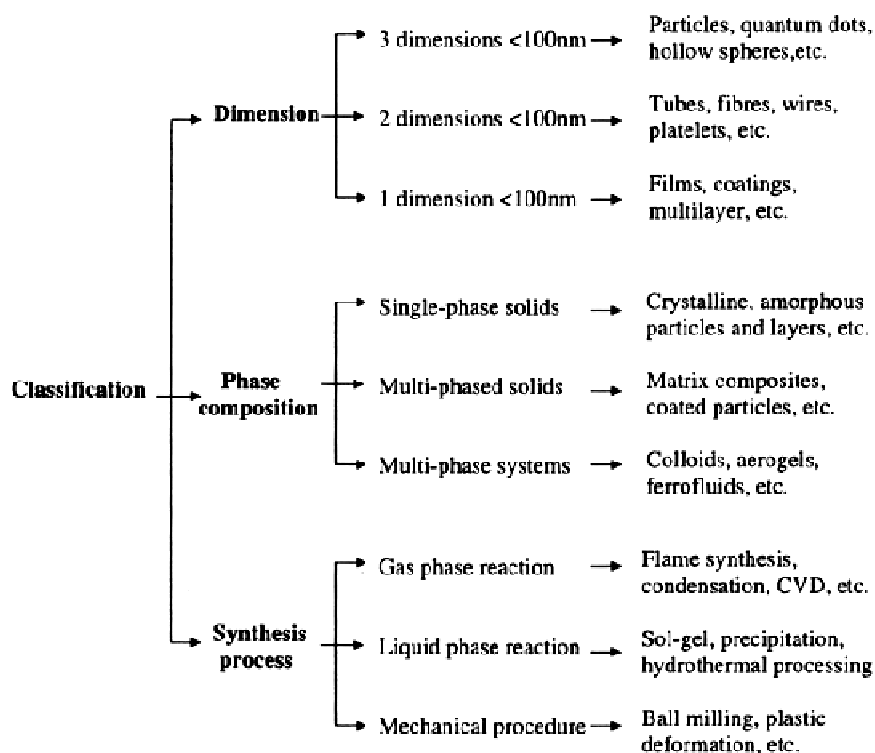


Figure (1) - Classification of synthesis of nanoparticles

Different analytical grade chemicals have been used for co-precipitation reaction of inorganic precursors of  $\text{Zn}^{2+}$  and  $\text{Se}^{2-}$  in aqueous medium containing the capping molecules of PVP. 0.02 M of zinc acetate has been dissolved in 50 ml of distilled water to obtain 0.02 M solution. 0.02M of  $\text{Na}_2\text{SO}_3$  has been dissolved in 50 ml of distilled water to get 0.02 M of solution and Se metal of 78.96 mg is added in this solution, the constant stirring of Se powder and  $\text{Na}_2\text{SO}_3$  made at 40 degree centigrade for 30 minutes. In the synthesis of ZnSe, the capping agent PVP was added to avoid agglomeration of grown nanoparticles. A colloidal suspension was obtained immediately after freshly prepared filtered solution of  $\text{Na}_2\text{SeSO}_3$  mixed with zinc acetate solution drop by drop with constant stirring. The precipitates were separated by 2000 rpm centrifugal machine and washed several times with distilled water. Then the sample was dried in atmospheric temperature over glass plate in natural air.

## RESULTS AND DISCUSSION

### X-ray diffraction pattern of the prepared ZnSe:Cu sample

ZnSe has two types of crystal phase, cubic and hexagonal phase. The wet chemical methods are applied to synthesize ZnSe nanoparticles. Phase identification using X-ray diffraction relies mainly on the positions of the peaks in a diffraction profile and to some extent on the relative intensities of these peaks. The shapes of the peaks however contain additional and often valuable information. The shape, particularly the width, of the peak is a measure of the amplitude of thermal oscillations of the

atoms at their regular lattice sites. It can also be a measure of vacancy and impurity element concentrations and even plastic deformation-any factor which results in a distribution of d-spacing.

Crystallite size can also cause peak broadening in terms of incident beam divergence which makes it possible to satisfy the Bragg condition for non-adjacent diffraction planes. Once instrument effects have been excluded, the crystallite size is easily calculated as a function of peak with by equation (1) specified as the full width at half maximum peak intensity (FWHM), peak position and wavelength.

X-ray diffraction pattern of ZnSe sample is shown in Figure 2. The several peaks of ZnSe have been obtained due to diffraction from different planes of ZnSe. The information on the particle size (A) of ZnSe:Cu nanoparticles has been obtained by the following Scherrer relations<sup>18</sup>

$$A = 0.9 \lambda / \beta \cos \theta \quad (1)$$

where  $\beta$  is the full-width-half-maximum (FWHM) of the diffraction peaks.

The crystalline nature of the nanoparticles with different concentration of capping agent & impurity determine when XRD patterns were studied. X-ray diffraction pattern have been obtained by Bruker D8 advance. X-Ray diffractometer with irradiation from copper  $K\alpha$  line ( $K\alpha=1.5418 \text{ \AA}$ ). The nanoparticles were slow scanned between  $0^\circ$  to  $50^\circ$ .

The X-ray diffraction studies have been undertaken to determine their crystal structure & crystalline size. Figure (2) shows the diffraction patterns of ZnSe:Cu nanocrystals for different PVP concentration.

From the figure major peaks are obtained in all the samples, which indicate that all the samples have cubic phase with Zinc blentz structure.

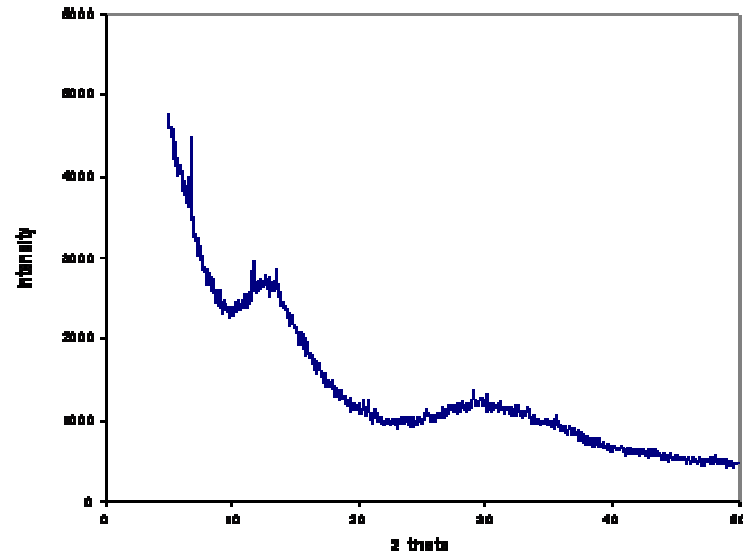


Figure 2(a)-XRD of ZnSe:Cu at 0M cons. of PVP

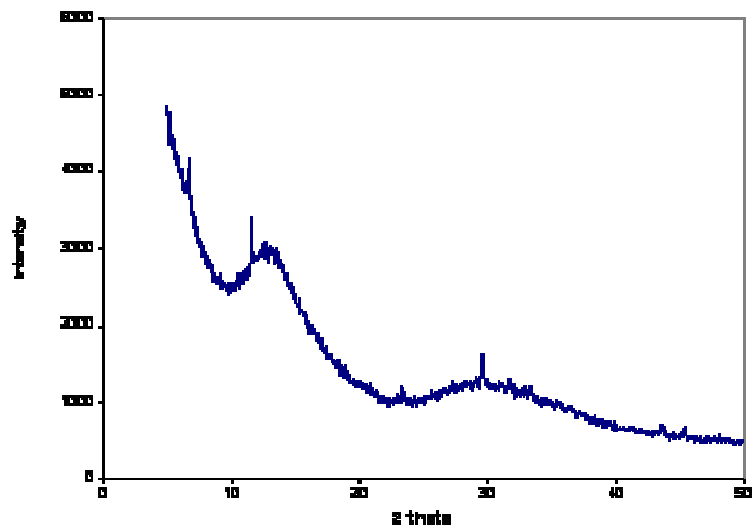


Figure 2(b)-XRD of ZnSe:Cu at 0.005M cons. of PVP

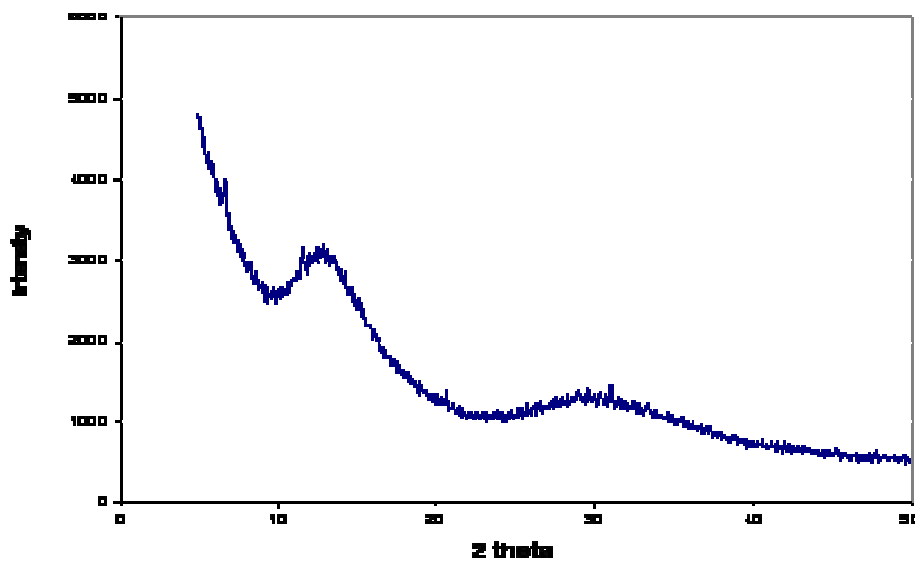


Figure 2(c) -XRD of ZnSe:Cu at 0.01M cons. of PVP

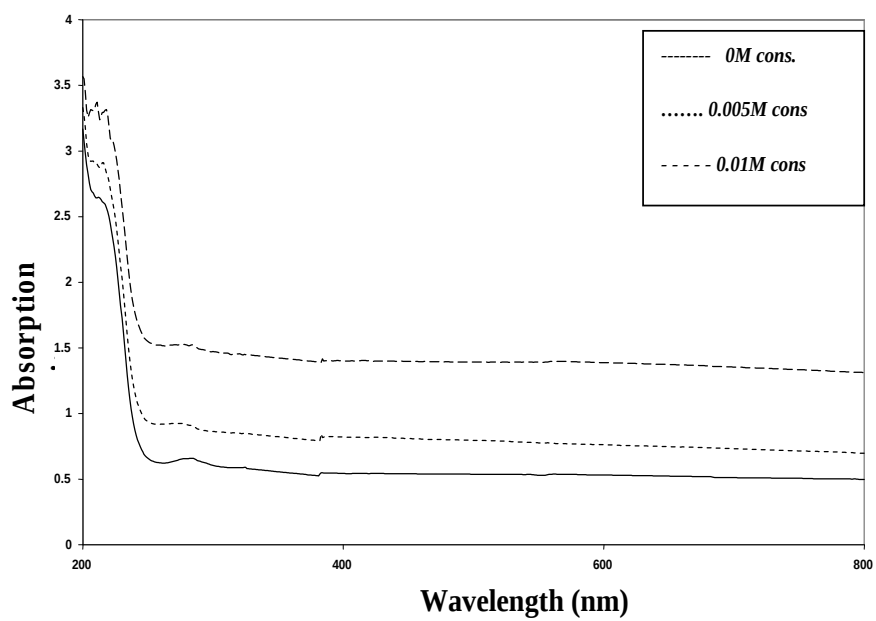


Figure 3- Absorption spectra for different PVP concentration

### Optical studies

The optical properties of ZnSe:Cu nanoparticles are dependent on the size and the shape of the QDs. The optical properties of ZnSe:Cu nanoparticles were characterized by UV-Vis absorption and photoluminescence spectra. The absorption spectra of ZnSe are shown in Figure 3. There is a obvious shoulder edges in the UV-Vis absorption spectrum. The absorption spectra of ZnSe:Cu nanoparticles were studied without taking into account the reflection and transmission losses.

The absorption data were analyzed using the classical relation for near edge optical absorption of semiconductors.

$$\alpha = [\alpha_0 (h\nu - E_g)^n / h\nu] \quad (2)$$

where  $\alpha_0$  is a constant,  $E_g$  is the energy separation between bottom of the conduction band and top of the valence band,  $h\nu$  is photon energy, and  $n$  is constant. For allowed direct transition  $n=1/2$  and allowed indirect transition  $n=2$ . The band gap energy  $E_g$  is determined by extrapolating the linear portion of the curve to the energy axis at  $\alpha = 0$ .

The band gap energy  $E_g$  of ZnSe nanoparticles was found to be 3.14 eV that showed the 'blue shift' of 0.44 eV from standard bulk band gap at room temperature ( $E_g = 2.7$  eV). It is well-known that the reaction conditions such as heating time, temperature, kinds and amount of reagents have effect on the morphology and size of the products in the processes.

### Size Quantization effect

Quantization of ultrafine particles arises from the confinement of charge carriers in semiconductors with potential wells of small dimensions (less than the De Broglie wavelength of the electrons and holds). Under these conditions, the energy levels available for the electrons & holes in the semiconductor and valence bands become discrete.

As a consequence, the relative energy and band gap spacing of the discrete highest occupied and lowest unoccupied molecular orbitals in nano-semiconductor increases and the partial size decreases with increase of capping agent concentration which can be understood as the effect of the size quantization. Figure 4 illustrate the effect of the size quantization.

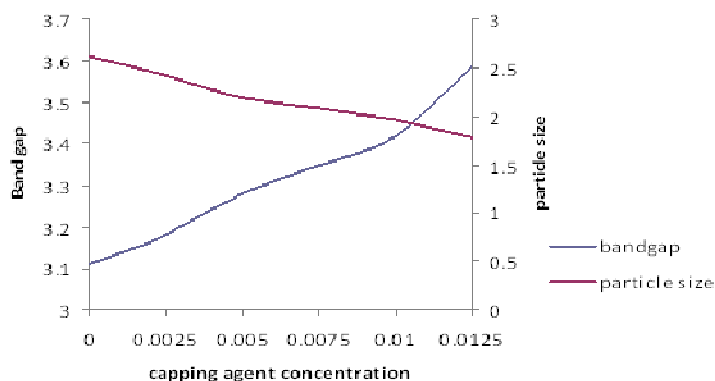


Figure 4 - Graph between particle size and band gap for various Concentration of capping agent

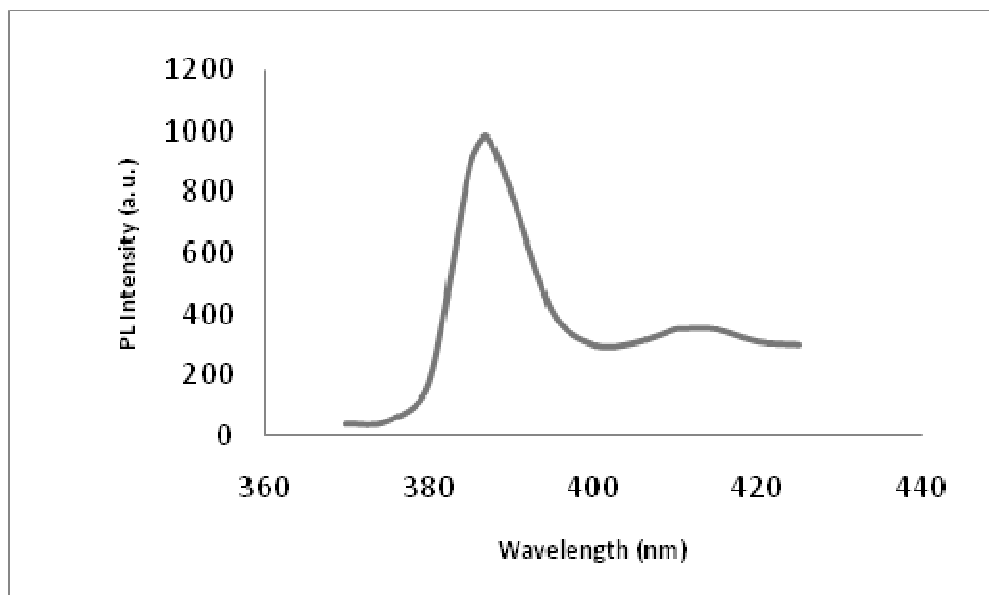


Figure 5 - Photoluminescence spectra of the ZnSe:Cu Sample at 0M PVP

### Photoluminescence Spectra

For measurement of the photoluminescence, the samples were deposited on the cello tape and the slide was fixed onto entrance slit of the monochromator. A 250 nm filter was placed between the UV lamp and the samples for exciting photoluminescence. By rotating the drum of monochromator, the wavelength at the exit slit has been varied from 300 nm to 800 nm and thus relative PL intensity at different wavelengths has been measured, and subsequently the PL spectra are obtained.

The room temperature PL spectrum centered at 387 nm of as prepared ZnSe:Cu nanoparticles is shown in Figure(5), which is attributed to the recombination of excitons

and the UV- blue emissions at about 410 nm which results from the recombination of a photon-generated hole with a charge state of the specific defect.

### CONCLUSION

ZnSe nanoparticles has been prepared in aqueous solution of zinc acetate and sodium seleno sulphate at room temperature. PVP in defined amount of water play important role in formation of ZnSe nanoparticles. It served not only as reduction agent which helps to dissolve Se in the mix solvent but also as a complexing agent, shape controller and as the stabilizing agent. ZnSe nanoparticles size confirmation is done by XRD and strong blue shift was observed in UV-Vis analysis of the sample.



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